# SPECTROGRAPHIC ANALYSES OF PLANT MATERIAL

BY
RUSSELL JOHN KEIRS
B.S., University of Illinois, 1937
M.S., University of Illinois, 1938

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

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## SPECTROGRAPHIC ANALYSIS OF PLANT MATERIAL

### Introduction

A nutritional study of plant growth, involving the limitation of the nutrients to a definite area of the root system and the determination of the effect of this type of feeding upon the foliage, required sensitive and rapid methods for the estimation of the elements in very small samples. This need gave rise to the present study of the application of spectrographic methods to this problem.

If a substance is subjected to proper excitation conditions, the intensities of certain lines or regions of the spectrum will be a function of the amounts of the elements present. This fact is the basis for spectrographic methods. Hence, quantitative spectrographic analysis is concerned, (1) with the establishment of proper excitation conditions, (2) with the resolution and selection of the spectral lines or regions for observation and (3) with suitable methods for evaluation of the intensity of the selected region as a function of concentration.

Since the compounds of the essential mineral elements in the ash of plants are soluble in water, and since a number of advantages are inherent in solution procedures, the investigation was limited to samples of this nature.

Several methods for solution analysis have been described in the literature.[2, 3, 4] Each has its individual merits and disadvantages as to ease of manipulation, complexity of design, adaptability to available electrode stand design, reproducibility of excitation conditions, and quantity of solution needed for an analysis.

### Experimental

In the preliminary work, the use of carbon electrodes impregnated with solutions of the various salts was found to be unsatisfactory because of the inability to control the penetration of the solution into the electrodes and to maintain constant excitation conditions.

A technique of excitation of the spectra which involved a slow regulated flow of the solution through a hollow carbon electrode into

a high potential spark was developed and very satisfactory results were obtained using it.

*Electrode System*

The lower electrode was an ordinary spectrographic carbon rod with a flat end surface exposed to the spark. The upper carbon electrode was constructed from a piece of 0.25-inch spectrographic carbon rod 1.25 inches long. One end of the electrode was drillel to a depth of 1-inch with a 0.11-inch drill. The size and depth of drill were chosen to fit the particular size to which the glass capillary end was drawn. The remaining 0.25-inch of the electrode was drilled with a 0.08-inch drill. The smaller hole was necessary to effect a steady flow of solution into the spark and to prevent large drops from playing upon the spark and varying excitation conditions.

The device for introducing the solution, a "dropping electrode," was constructed from a piece of glass tubing 0.25-inch in diameter, 7 inches long, and fitted with a stopcock at one end. The other end was softened in a flame and drawn to a pointed capillary. The capillary tip was then fire-polished until the orfice permitted a flow of approximately 0.9 cc. per minute, when the stopcock was adjusted to the maximum opening. Since corrosive liquids were used, a shield made from blotting paper protected the electrode stand from spray.

*Equipment*

A Bausch and Lomb large Littrow spectrograph was employed, using a slit width of 60 to 70 microns and 4-mm. height. Appropriate prism positions were used to cover the section of spectrum to be examined. Excitation of the sample was obtained by a high-potential spark supplied from a 220-volt source, with sufficient resistance to produce a current of 17.5 amperes in the primary of a 1000 to 1, 5-kw. transformer. The secondary circuit consisted of 8 condensers (in parallel) of 8.5 x $10^{-4}$ microfarad each. No inductance coil was used in the secondary circuit.

Eastman D.C. (double coated) orthochromatic plates were used and processed in Eastman standard X-ray developer and fixer. A Gaertner visual microdensitometer and a Leeds and Northrup recording microphotometer were used to evaluate line densities.

*Quantitative Procedures*

Procedures for the estimation of manganese, magnesium, phosphorus, calcium, iron and potassium, utilizing the internal standard principle were formulated. The comparison lines selected and ranges of concentration at which the determinations were made are as follows:

| Range of conc. mg. per ml. | "Unknown" Element A.U. | "Standard Element A.U. |
|---|---|---|
| Mn—0.001-0.25 | Mn-2576.1 | Cu-2369.8 |
| Mg—0.100-5.00 | Mg-2779.2 | Cu-2824.4 |
| Fe—0.001-3.00 | Fe-2739.5 | Ni-2821.3 |
| P —0.040-1.00 | P -2536.4 | Cu-2492.2 |
| Ca—0.008-0.10 | Ca-3158.9 | Ni-3101.9 |
| K —0.100-0.25 | K -7664.9 | Zn-4180.1 |

Manganese, magnesium, iron and phosphorus were determined simultaneously. Calcium and potassium required separate determinations.

Several methods of handling data were studied and the results compared.[1] It was found that the use of an internal standard was essential for the best results. Plate calibration was found unnecessary when plates of the same lot were employed. Under these conditions the use of plate calibration curves actually decreased the precision of the analyses.

The presence of phosphorous was found to have an inhibiting effect upon the line densities of other elements present. However, when nickel was employed as the internal standard, the effect was proportionally the same on the lines of nickel and those of the elements being estimated. Hence, in the final analysis no increase in error was observed.

An examination was also made of the effect of sodium, particularly upon the density of the potassium line. Its presence in the solution in the range of relative concentrations to be anticipated in plant ash had a negligible influence.

It is believed that the general procedure which has been developed

will be found convenient and satisfactory for many other analyses in which the samples may be easily brought into solution.

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## Publication


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## VITA

The author was born in Springfield, Illinois, on August 27, 1915. He attended the Springfield grammar schools until 1929 and graduated from the Springfield High School in 1933. His undergraduate work was done at the University of Illinois from which he received the degree of Bachelor of Science in Chemistry in 1937. In 1938 the University of Illinois awarded him the degree of Master of Science in Chemistry. He held a teaching assistantship in the chemistry department at the University of Illinois from September, 1938 until 1941.

He is a member of Sigma Xi honorary society.

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